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(54) **Process for cracking waste rubber tires**

Verfahren zum Cracken von Altreifen

Procédé de craquage de pneumatiques usés

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Description

The present invention relates to a process for cracking waste rubber tires.

Conventional waste tires may be crushed or pulverized for producing reclaimed rubber which is used in limited proportions as an extender to lower the cost of rubber products. It may be somewhat deleterious to the final physical properties of the rubber product, but it aids in the processing because it flows and extrudes readily. However, the reclaimed rubber generally accounts for a low percentage such as about 10% of rubber consumption in the United States. For environmental protection, it is necessary to treat the waste rubber tires not used in the above-mentioned reclaiming processes.

Several conventional cracking processes are therefore applied for treating the rapidly growing waste rubber tires for producing fuel oils and gases by cracking the waste rubber tires, of which a conventional process discloses a cracking reaction conducted at a high temperature of more than 1000°C under a high pressure of 3 - 30 kilograms per square-centimeter. However, such a conventional cracking process for cracking waste rubber products at high temperature and pressure may have the following drawbacks:

1. A high initial cost is required for installing the high pressure vessel at higher reaction temperature.
2. Since many flammable gaseous products, such as: hydrogen, low-carbon hydrocarbon gases including methane, ethane, propane, butane, isobutane, butene, etc., may be produced during the cracking process, such flammable gases produced from the high temperature, high pressure reactor will be very dangerous or hazardous to the working environment in view of industrial safety factor. For instance, the hydrogen gas has an ignition temperature of 1085°F (585°C); methane of 999°F (537°C); ethane of 959 °F (515°C), etc. They are all flammable, or easily explosive once leaked from the high-temperature cracking reactor and should be handled or treated very carefully, thereby increasing operation complexity and cost therefore.
3. It will consume much energy to conduct the cracking reaction at higher temperature, thereby wasting valuable energy resources.

Therefore, the present inventor invents a process for cracking waste rubber tires at lower temperature and pressure for overcoming the drawbacks of conventional cracking processes.

According to the present invention, there is provided an economic and safe process for cracking waste rubber tires and rubber products by catalytic cracking of the rubber tires and rubber products in the presence of a mica catalyst of sericite at a reaction temperature of 230° - 400°C under a pressure of 1 - 2.5 atmospheres to form oils, carbon black, gaseous products, and other residual products.

The present invention will be further described with reference to the accompany drawing, in which:

The single drawing figure shows a process flow sheet for cracking waste rubber tires in accordance with the present invention.

As shown in the single drawing figure, the present invention comprises a process for cracking waste rubber tires and rubber products by the following procedures:

- a. Washing the waste rubber tires or the like (1) such as by water washing (2); (Note: The "waste rubber tires or the like" may include used tires, any kind of rubber tires, inner tubes, and other rubber products, etc.)
- b. Crushing (2) the washed waste rubber tires into rubber scraps or chips having a size of about 5 cm X 5 cm per piece;
- c. Mixing (3) the rubber scraps with pulverized catalyst of mica in a mixer and preheating the mixture to 210°C;
- d. Cracking (4) the mixed rubber scraps with micas catalyst in a closed reactor for performing destructive distillation under heating to keep a temperature ranging from 230°C to 400° C and under a pressure of 1 - 2.5 atmospheres. The cracking reaction is started at 230°C, while the cracking proceeds rapidly and vigorously at 350°C. The maximum reaction temperature may reach up to 400°C. The pressure 1 - 2.5 atm. is a systematic reaction pressure created in situ in the reactor by the gases produced during the cracking reaction, without being blanketed by any inert gas such as nitrogen gas in the reactor;
- e. Condensing and separating the vapor-phase products (5) into gaseous products (51) and mixed oils (52) which may be further separated by fractional distillation (7), into oils including: light oil and gasoline (71), kerosene (72), diesel oil (73) and heavy oil (74); and
- f. Separating the solid products (6) from the cracking step (4) into carbon black (61), steel wires (62), and other residue products (63).

The mica catalyst used in this invention is sericite.

Sericite has a chemical formula of $KAl_2(AlSiO_3O_{10})(OH)_2$, with the following chemical composition (100% by weight):

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SiO ₂	47.65
Al ₂ O ₃	37.03
K ₂ O	9.02
TiO ₂	0.10
Fe ₂ O ₃	0.01
MgO	0.04
Na ₂ O	0.76
H ₂ O	0.73 - 4.97
P ₂ O ₅	0.02
FeO, MnO and CaO	Trace

The catalyst quantity used in this invention is 2 - 3 % by weight based on 100% of waste rubber tires and products. The mixed oil products includes: light oil, gasoline, kerosene, diesel, and heavy oil, and may be directly served as fuel oil without further fractionation. However, if necessary, the mixed oils may be further separated into each specific oil by fractional distillation.

The gaseous products include hydrogen, hydrocarbons of low carbon atoms including methane, propane, butane and butene, carbon monoxide, carbon dioxide, and trace of other products or sulfur product. The sulfur product is present because sulfur was added during the vulcanization of rubber tires manufacturing. The gaseous products can also be used as a fuel. However, the isobutylene and butylene primarily existing in the gaseous products may be further isolated for its industrial use, such as for producing butyl rubber.

The waste rubber tires may be selected from rubber tires having steel wires lined in the tires, inner tubes of tires, or other waste rubber products including natural and synthetic rubbers. If steel-belted rubber tires are treated in this invention, steel wires may be produced in the solid products after destructive distillation of the reactants.

The present invention will be further described in detail in the follow examples:

Example 1

In a 32 liters autoclave provided with intermittently operating agitator, 6680 grams of crushed inner tubes of rubber tires (scraps, each of 5 cm X 5 cm) and 150 grams of sericite catalyst were added. The autoclave is gradually heated to a temperature of 230°C for starting the cracking reaction. The reaction temperature is kept in the range of 230 - 400°C under a closed systemic pressure of 1 - 2.5 atm. (absolute pressure) for one hour.

After finishing the cracking process, a plurality of products are obtained as shown in Table 1.

Table 1

Products	Weight (grams)	weight, %
Gaseous products	1400	21
Mixed oils	2280	34
Carbon black and residue	2850	43
Water	150	2

The mixed oils are further treated with fractional distillation to produce each specific oil as listed on Table 2.

Table 2

Oil (Distribution Temperature range)	Weight (grams)	Weight, %
Light Oil, 50 - 186°C (fractional distillation at normal pressure)	370	16
Gasoline, 140 - 156°C (under vacuum, 500 mm Hg)	376	16.6
Kerosene, 156 - 180°C (500 mm Hg Vac.)	310	14

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Table 2 (continued)

Oil (Distribution Temperature range)	Weight (grams)	Weight, %
Diesel, 180 - 200°C (500 mm Hg Vac.)	810	36
Heavy Oil	385	17.4

The gaseous products are analyzed and identified to have a composition as shown in Table 3.

Table 3

Gases	100%, Percentage by volume
Hydrogen	12
Methane	20.59
Ethane	4.42
Ethylene	1.07
Propane	2.85
Propylene	1.66
iso-butane	5.13
iso-butylene and Butylene-1	45.3
Butylene-2	0.04
n-pentane	0.15
Pentylene	0.49
CO ₂	4.54
CO	1.65

The iso-butylene and butylene-1 has a volume percentage of 45.3 based on the total gaseous products, which can be further isolated to be valuable industrial products.

Example 2

Repeat the procedures as shown in Example 1 by substituting the inner tubes of rubber tires with steel belted rubber tires, the crushing products are obtained as shown in Table 4, wherein the results obtained from Example 1 are listed for comparison.

Table 4

Products	Example 2	Example 1
Gaseous products	12%	21%
Mixed Oils	50%	34%

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Table 4 (continued)

Products	Example 2	Example 1
Carbon black and residue	32%	43%
Water	2%	2%
Steel wires	4%	-

From the data as listed in Table 4, the steel belted rubber tires (having steel wires) will produce more oils, but less gaseous products, than that as cracked from the inner tubes of tires (without steel wires).

Comparatively, the fractionated oils further separated from the "mixed oils" either in Example 1 or 2 are almost equal in composition (weight) percentage as shown in Table 5, indicating that the cracking products obtained from the process of the present invention can provide stable and useful fuels. Therefore, the present invention may enhance the reuse of energy resources for preventing wasting of rubber tires, since the rubber tires are convertible to be useful and valuable fuel oils, gaseous products and carbon black.

Table 5

Oils	Example 1	Example 2
Light oil/gasoline	32.6	33
Kerosene	14	15.5
Diesel	36	35
Heavy Oil	17.4	16.5

Accordingly, this invention provides a cracking process for treating waste rubber tires to produce useful products with the following advantages superior to conventional rubber cracking processes:

1. Cracking is performed at low temperature and low pressure for a safer reaction condition. For example, the maximum reaction temperature, 400°C, is much lower than the ignition temperature of hydrogen, methane, and ethane as aforementioned, providing a safer condition.
2. Low installation, operation and maintenance cost and low energy consumption will be effected by this invention because of its low temperature and pressure reaction conditions.
3. Air pollution can be effectively prevented since the lower reaction pressure will minimize the possibility of gas leakage of the dangerous gases from the reactor and process system.

The present invention may be modified without departing from the spirit and scope as claimed in this invention. Other polymers of high molecular weight can also be cracked by using the process as described in this invention.

Claims

1. A process for cracking waste rubber tires comprising:

- a. washing and crushing waste rubber tires into rubber scraps;
- b. mixing the rubber scraps with a catalyst of sericite under preheating to 210°C;
- c. performing a cracking reaction with destructive distillation of the rubber scraps in the presence of the catalyst of sericite comprising a catalyst quantity of 2 - 3% by weight based on 100% of total waste rubber tires fed in the cracking reaction under heating to maintain a temperature ranging from 230°C to 400°C under a pressure of 1 atmosphere to 2.5 atmospheres for one hour to produce cracking products of vapor-phase products containing gases and mixed oils, and solid products containing carbon black and residual products; and
- d. separating the cracking products into gases, mixed oils, carbon black and residual products.

2. A process according to Claim 1, wherein said mica catalyst is a sericite powder.

Patentansprüche

1. Verfahren zum Cracken von alten Gummireifen, umfassend:

- 5 a) Waschen und Zerkleinern von alten Gummireifen zu Gummischnitzeln;
b) Vermischen der Gummischnitzel mit einem Sericit-Katalysator und Vorerhitzen auf 210 °C;
c) Durchführen einer Crack-Reaktion mit zerstörender Destillation der Gummischnitzel in Gegenwart des Se-
ricit-Katalysators, mit einer Katalysatormenge von 2 - 3 Gew.-%, bezogen auf 100 % der Gesamtmenge an
10 der Crack-Reaktion zugeführten alten Gummireifen unter Erhitzen, um eine Temperatur im Bereich von 230
°C bis 400 °C beizubehalten, unter einem Druck von 1 atm bis 2,5 atm für eine Stunde, zur Erzeugung von
Crack-Produkten aus Dampfphasenprodukten, die Gase und Mischöle enthalten, sowie festen Produkten, die
Ruß und Rückstände enthalten; und
d) Auftrennen der Crack-Produkte in Gase, Mischöle, Ruß und Rückstände.

15 2. Verfahren nach Anspruch 1, worin der Glimmerkatalysator ein Sericitpulver ist.

Revendications

20 1. Procédé de craquage de pneumatiques usés comprenant :

- a. Le lavage et le broyage des pneumatiques usés en déchets de caoutchouc ;
25 b. Le mélange des déchets de caoutchouc avec un catalyseur de séricite avec préchauffage à 210°C ;
c. L'accomplissement d'une réaction de craquage avec distillation destructrice des déchets de caoutchouc en
présence du catalyseur de séricite comprenant une quantité du catalyseur de 2 - 3 % en poids, en se basant
sur 100 % de pneumatiques usés totaux fournis dans la réaction de craquage sous chauffage pour maintenir
30 une température comprise entre 230°C et 400°C sous une pression de 1 atmosphère à 2,5 atmosphères
pendant une heure pour produire des produits de craquage des produits en phase vapeur contenant des gaz
et des huiles mélangées et des produits solides contenant du noir de carbone et des produits résiduels ; et
d. La séparation des produits de craquage en gaz, huiles mélangées, noir de carbone et produits résiduels.

35 2. Procédé selon la revendication 1, où ledit catalyseur de mica est une poudre de séricite.

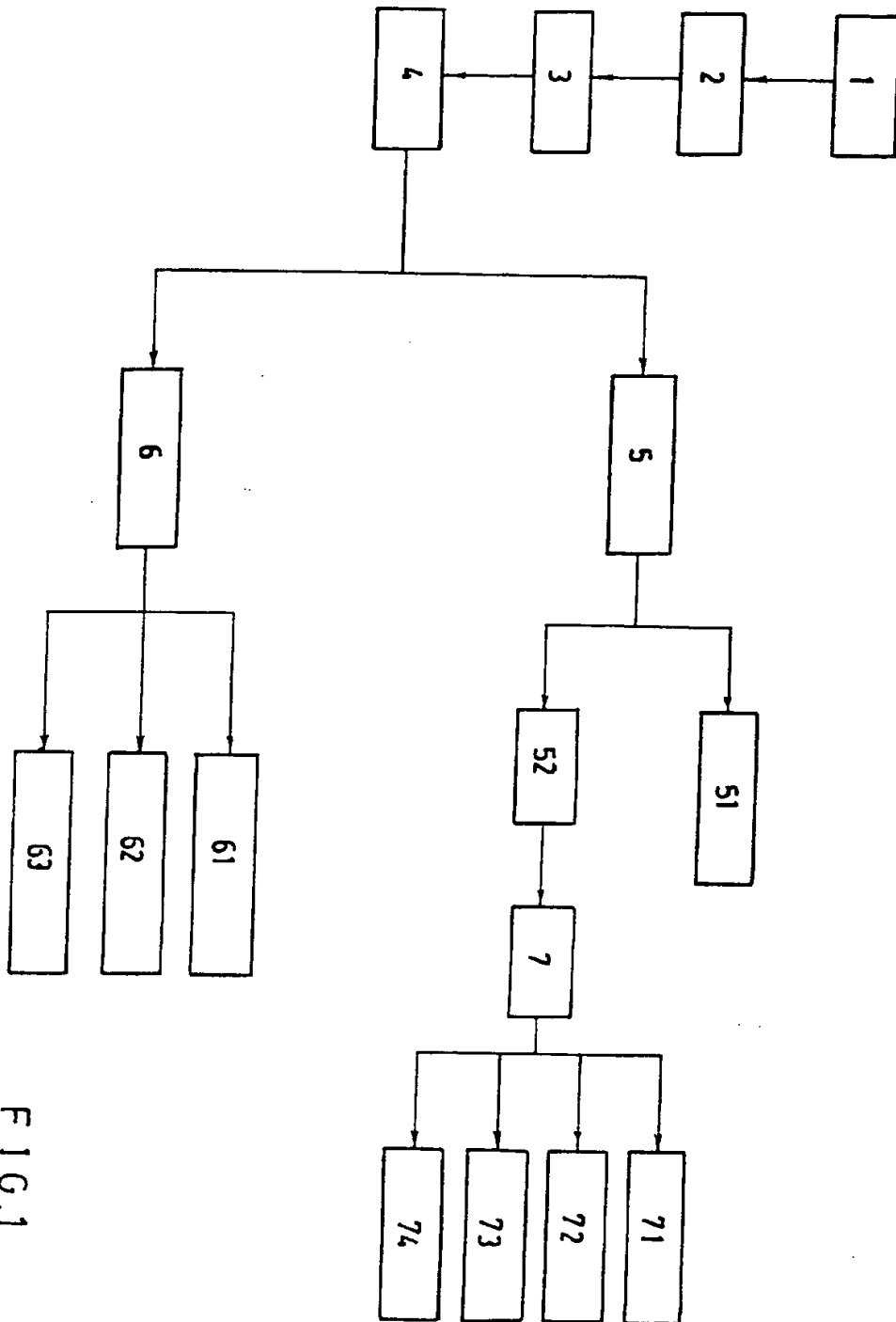


FIG. 1